

Palladium-catalyzed carbopalladation and carbocyclization of arynes with aryl halides: a highly efficient route to functionalized triphenylenes†

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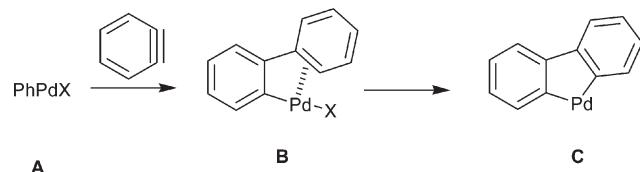
Highly substituted triphenylene derivatives were prepared in good yields *via* the palladium-catalyzed carbocyclization of arynes with aryl iodides.

Triphenylenes are the most widely-synthesized and studied discotic mesogens.¹ Recently, these materials have been discussed as potential candidates for opto-electronic devices.² Several research groups have worked on the synthesis of symmetrical, unsymmetrical and functionalized triphenylene for discotic liquid crystals.³ Moreover, the interest shown by many research groups over the years clearly signifies the importance of substituted triphenylenes in materials chemistry.⁴ Among the recent developments in the synthesis of triphenylenes, the use of highly reactive arynes in palladium-catalyzed trimerization is a very notable method.⁵ However, the method was useful only for the synthesis of symmetrical triphenylenes. In addition to the preparation of triphenylenes, arynes have been used to prepare a variety of fused polyaromatics. Palladium-catalyzed cocyclotrimerization of alkynes and benzyne or allenes and benzyne (alkyne– or allene–benzyne–benzyne), leading to phenanthrene derivatives, have been reported by Castedo's, Yamamoto's and our groups.⁶ Castedo *et al.* described a synthesis of benzotriphenylenes.⁷ Furthermore, they also reported an intramolecular [2 + 2 + 2] cyclotrimerization of benzyne with suitably functionalized benzo-diyne to give benzo[*b*]fluorenones.⁸ Recently, we also reported a synthesis of benzo[*b*]triphenylenes *via* deoxyaromatization of the product obtained from [2 + 2 + 2] cocyclotrimerization of arynes with bicyclic alkenes.⁹

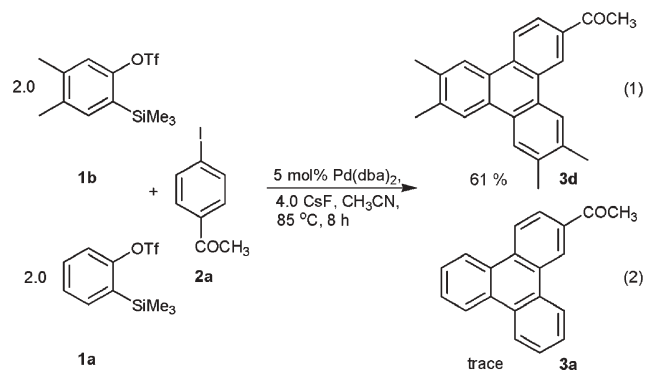
It is well known that all of the above palladium-catalyzed cocyclotrimerization reactions proceed mechanistically *via* a 5-membered ring palladacycle. We envisaged that a similar palladacycle **C** (Scheme 1) could be generated from an insertion

of aryne into an arylpalladium intermediate **A** and subsequent cyclopalladation. It is also understood that a judicious selection of reaction conditions is required to activate the C–H bond while at the same time maintaining the conditions necessary for a steady generation of aryne.¹⁰ Treatment of 2-(trimethylsilyl)-4,5-dimethylphenyl triflate (**1b**) (2 equiv.) with 4-iodoacetophenone (**2a**, 0.30 mmol) in the presence of 5 mol% Pd(dba)₂ and CsF (4 equiv.) in CH₃CN at 85 °C for 8 h gave the expected unsymmetrical triphenylene product (Scheme 2) in 61% yield.¹¹ We also found that arynes **1b** reacted with various aryl iodides bearing an electron-withdrawing group to give moderate yields (50 ~ 60%) of the expected triphenylene products along with the cyclotrimerization product of aryne **1b**. To our surprise, when benzyne precursor **1a** was used instead of **1b**, the reaction gave only a trace of the expected triphenylene product **3a** (Scheme 2). Similarly, the reaction of other aryl iodides with **1a** also afforded only a trace of the expected products. The cyclotrimerization product triphenylene from **1a** was instead the major species observed. Thus, under the reaction conditions used, it appears that the reaction is extremely sensitive to the aryne substrates. To obtain more reliable reaction conditions which can be used for various arynes, we chose to find a suitable additive rather than undertake an ordinary manipulation of the reaction conditions. No desired product was obtained when silver salts (AgBF₄, AgNO₃, AgOAc or Ag(O₂CCF₃)) were added to the reaction solution. The use of Et₃N gave the expected product **3a** in only 6% yield. Interestingly, the use of 1.2 equiv. of Tl(OAc) remarkably improved the yield of **3a** up to 72%. Moreover, **3d** was obtained from **1b** and **2a** in 83% yield (Table 1, entries 1 and 5).¹²

Table 1 summarizes the results of the reactions of various aryl iodides with arynes under reaction conditions similar to those of



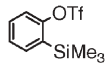
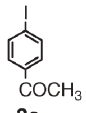
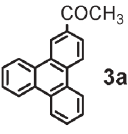
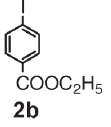
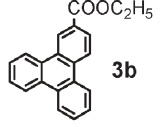
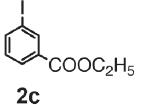
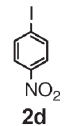
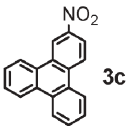
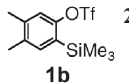
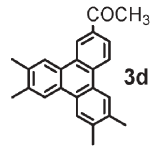
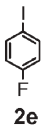
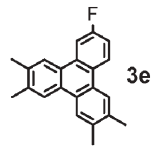

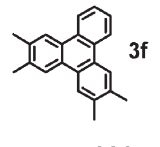
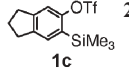
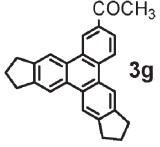
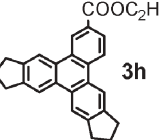
Scheme 1



Scheme 2

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† Electronic Supplementary Information (ESI) available: General experimental procedures, spectral data for all compounds, ¹H and ¹³C NMR spectra for all compounds. See DOI: 10.1039/b515846j

Table 1 Results of the Pd-catalyzed carbocyclization of arynes **1** and aryl halides **2**^a

Entry	1	2	Product 3	Yield (%) ^b
1				72
2	1a			81
3	1a		3b	79
4	1a			78
5		2a		83
6	1b			82
7	1b			75
8		2a		73
9	1c	2b		77

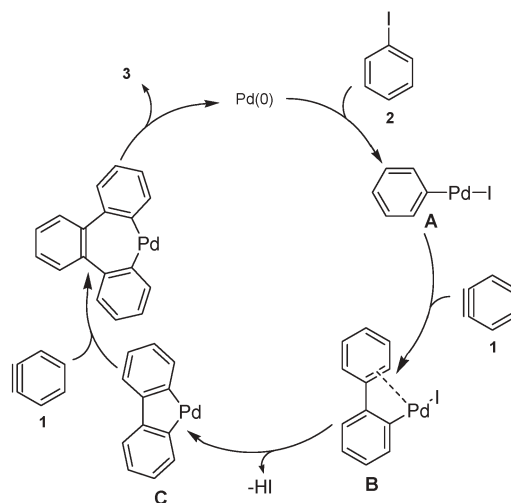
^a Reaction conditions: 0.60 mmol of benzyne precursors **1**, 0.30 mmol of arylhalide **2**, 0.015 mmol of Pd(dba)₂, 1.20 mmol of CsF, 0.36 mmol of Ti(OAc)₄, under nitrogen in 3.0 mL of CH₃CN at 85 °C for 8 h. ^b Isolated yields.

Table 1, entry 1. When 4-iodoethylbenzoate (**2b**) was treated with **1a**, triphenylene-2-ethylcarboxylate (**3b**) was obtained in 81% yield (Table 1, entry 2). The reaction of 3-iodoethylbenzoate (**2c**) gave **3b** as the only isomer (Table 1, entry 3). It is interesting to note that both 4-iodoethylbenzoate and 3-iodoethylbenzoate gave the same

product in nearly the same yield. 4-Iodonitrobenzene (**2d**) afforded 2-nitrotriphenylene (**3c**) in 79% yield (Table 1, entry 4). The reaction of aryne precursor **1b** with 4-fluoroiodobenzene (**2e**) gave the corresponding fluorotriphenylene **3e** in 82% yield (Table 1, entry 6). The use of unsubstituted iodobenzene (**2f**) gave the tetramethyltriphenylene **3f** in 75% yield (Table 1, entry 7). Similarly, indanyl-substituted aryne precursor **1c** reacted with **2a** and **2b** to give the corresponding triphenylenes **3g** and **3h** in 73 and 77% yields, respectively (Table 1, entries 8 and 9). The present reaction conditions appear unsuitable for aryl iodides with an electron-donating group and benzynes with electron-withdrawing substituents. For example, no expected unsymmetrical triphenylene products were observed for the reaction of 4-iodoanisole with **1b** and 2-(trimethylsilyl)-4,5-difluorophenyl triflate with **2a** under the standard reaction conditions.

A plausible mechanism for the reaction of aryne **1** with aryl iodide **2** is illustrated in Scheme 3 (neutral ligands are omitted).¹³ The oxidative addition of **2** to the Pd(0) species gives arylpalladium(II) intermediate **A**. Coordination of benzyne to intermediate **A**, followed by insertion into the Ar–Pd bond, forms an *ortho*-biaryl palladium species **B**, in which the aryl group is η^2 -bonded to the palladium center. It is well known that η^2 -arene complexes are intermediates in the C–H activation of arene systems.¹⁴ Cyclopalladation through an intramolecular C–H activation affords a five membered palladacycle **C**. Further reaction of this intermediate with another benzyne and subsequent reductive elimination affords the corresponding annulated product with regeneration of the Pd(0) species. The possibility of insertion of two molecules of benzyne into **A** and the subsequent cyclopalladation to form a seven-membered palladacycle cannot be totally excluded. Although the role of thallium salts is not very clear at this stage, they are known to assist the removal of the halide from palladium complexes and enhance *ortho*-metallation.¹⁵

In summary, we have demonstrated that arynes can be efficiently employed in the palladium-catalyzed carbopalladation and cyclopalladation sequence directed towards the synthesis of polyaromatic compounds. While the present method is useful for the preparation of a variety of highly functionalized triphenylenes, its catalytic mechanism is not yet clear. A more detailed study of the effect on the reaction of substituents attached to the aryne

**Scheme 3**

moiety and the aryl iodide, and the isolation of reaction intermediates should be beneficial to understanding the detailed reaction mechanism. Further studies in these directions are currently under way.

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